

**Final Technical Report**

**on**

**Investigation of Selective Non-Catalytic Processes for In-Situ  
Reduction of NO<sub>x</sub> and CO Emissions from Marine Gas Turbines  
and Diesel Engines**

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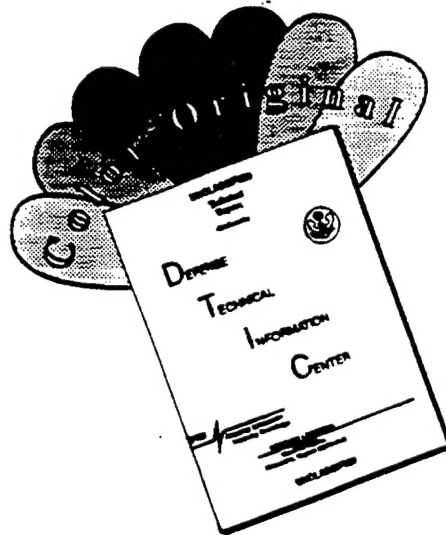
**Craig T. Bowman and Ronald K. Hanson**

**HIGH TEMPERATURE GASDYNAMICS LABORATORY  
Mechanical Engineering Department  
Stanford University**

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## 1.0 Summary

The effectiveness of selective non-catalytic (SNCR) gas-phase reaction processes for  $\text{NO}_x$  removal from combustion products at elevated pressures was investigated in a combined experimental and modeling research program. Calculations using existing chemical models for SNCR indicate that the temperature window for  $\text{NO}_x$  removal by SNCR widens as pressure increases, resulting in  $\text{NO}_x$  removal at higher temperatures than at ambient pressure. The calculations also show a significant reduction in the reaction time scale with increasing pressure. These observations suggest the possibility of utilizing SNCR for reducing  $\text{NO}_x$  emissions from marine gas turbines and Diesel engines by direct injection of a reductant species into the combustion chamber, possibly as a fuel additive. Initial experiments were carried out at atmospheric pressure to allow comparison with previous measurements in order to verify the experimental approach. Following these validation tests, experiments were conducted at elevated pressures. Results from these tests, confirm the model predictions that the SNCR window for  $\text{NO}_x$  removal widens as the pressure increases. In addition, a project was initiated, to develop compact, robust, solid-state microsensors for pollutant species for use in control systems for reduction of pollutant emissions. The sensor concept is based on integrated circuit fabrication technology that allows the integration of a metal-oxide sensor with associated electronic circuitry on a single chip. Initial efforts focused on development of a sensor for  $\text{NO}_x$ .

## 2.0 Introduction

Currently available combustion modifications to reduce  $\text{NO}_x$  emissions from power-generating gas turbines and Diesel engines cannot meet existing stringent  $\text{NO}_x$  emissions standards. For this reason, post-combustion methods for  $\text{NO}_x$  removal from combustion products have been developed that are applicable to both gas turbines and Diesel engines. Some of these methods are based on injection of a nitrogen-containing reductant into the combustion products. The reductant initiates a reaction sequence leading to  $\text{NO}_x$  removal. The  $\text{NO}_x$ -removal process may take place entirely in the gas-phase (in a process termed Selective Non-Catalytic Reduction, SNCR), or it may take place partly or entirely on the surface of a catalyst (in a process termed Selective Catalytic Reduction, SCR). At atmospheric pressure,  $\text{NO}_x$  removal occurs within a narrow temperature window centered about 1250K for SNCR and centered about 600K for SCR. Typical exhaust gas temperatures in gas turbines are too low to utilize SNCR for  $\text{NO}_x$  removal from the exhaust gas, so that only the more complex and expensive SCR technique may be used. Exhaust temperatures in some Diesel engines are sufficiently high so that either SNCR or SCR may be used for  $\text{NO}_x$  emissions reduction; but, frequently, an additive or an external heat source is employed to improve the performance of SNCR.

There are several disadvantages in using conventional SNCR or SCR for  $\text{NO}_x$  emissions reductions in naval powerplants. First, the reductant must be carried on board the vessel in a separate storage tank. Second, the exhaust ducting from the engine must be modified to accommodate reductant injection and possibly a catalyst bed, resulting in an increased

footprint for the overall powerplant. Third, an additional control system for the process is required.

Because of the high  $\text{NO}_x$ -removal efficiency and relative simplicity of SNCR, the possibility of applying SNCR to gas turbines and Diesel engines by direct injection of a reductant into the combustion chamber, where the pressures and temperatures are higher, should be investigated. If significant  $\text{NO}_x$  removal can be obtained for these conditions, then it may be possible to include the  $\text{NO}_x$ -removing species as a fuel additive, thereby simplifying the application of the process to existing powerplants.

Some strategies to reduce  $\text{NO}_x$  emissions, for example, partial premixing (Gore et al., 1995), flow forcing (Sivasegaram and Whitelaw, 1995) or chemical or plasma after-treatment processes (Gundersen et al., 1995) require a control system to achieve maximum effectiveness. A major component of such control systems is a sensor for  $\text{NO}_x$  in the exhaust gas. The signal from this sensor is used as feedback in the control system. Existing sensors for pollutant species, such as  $\text{NO}_x$  or CO, lack sensitivity and time response, and they often exhibit poor selectivity to the desired pollutant species. In addition, these sensors are expensive. Hence, there is a need for development of compact, robust, sensitive and inexpensive sensors for pollutant species for use in control systems for emissions reduction and compliance monitoring.

## **3.0 Background**

### **3.1 Emissions Reduction by SNCR**

Available chemical models for SNCR (Glarborg et al., 1994; Bowman, 1997) have been used to explore the effects of pressure, temperature, exhaust gas composition, reaction time-scale and reductant type on  $\text{NO}_x$ -removal efficiency. Figure 1 shows the principal reaction pathways for NO removal for several common SNCR additives. In all cases the process requires generation of radical species, usually OH, H, or O that drive the overall process. NO removal occurs by reaction of NO with a nitrogen-containing radical formed from the injected compound to produce either  $\text{N}_2$  or  $\text{N}_2\text{O}$ . The  $\text{N}_2\text{O}$  may subsequently react to form  $\text{N}_2$  or it may be emitted from the system. At sufficiently high temperatures, the injected nitrogen compound oxidizes to produce additional NO. At low temperatures, there is insufficient radical generation to sustain the process. Hence, there is a temperature window where SNCR is effective in reducing NO in the combustion products. Some of the NO in the combustion products may be converted to  $\text{NO}_2$  via reaction with the  $\text{HO}_2$  radical that forms at lower temperatures.

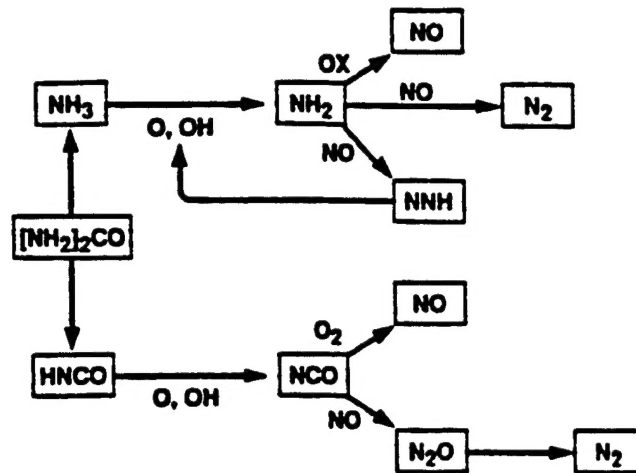


Fig. 1 Reaction path diagram illustrating the major steps in gas-phase NO removal by reaction with ammonia, isocyanic acid and urea (Bowman, 1997).

Figures 2 – 5 show typical results from simulations for two commonly used nitrogen-containing reductants, ammonia (NH<sub>3</sub>) and isocyanic acid (HNCO). At one atmosphere pressure, the calculated NO<sub>x</sub>-removal temperature window for NH<sub>3</sub> extends from 1200K – 1400K, Fig. 1. With increasing pressure, the calculated width of the NO<sub>x</sub>-removal temperature window increases. At 20 atmospheres pressure, the window extends from 1200K – 1550K. Also shown on Fig. 1 is a typical operating line of a marine gas turbine, indicating the possibility of significant reductions of NO<sub>x</sub> emissions from gas turbines by in-situ SNCR.

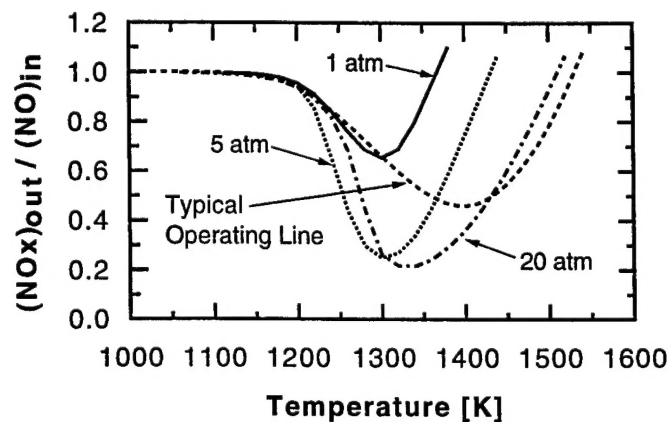


Fig. 2 Calculated reduction in NO<sub>x</sub> (NO + NO<sub>2</sub>) in combustion products as a function of temperature and pressure for added NH<sub>3</sub>. Initial NO = 250 ppm; initial NH<sub>3</sub> = 500 ppm; O<sub>2</sub> = 10%; reaction time = 10 ms. A typical gas turbine operating line is shown on the plot.

Smith and Caton (1995) have reported measurements of  $\text{NO}_x$  removal with  $\text{NH}_3$  injection where total  $\text{NO}_x$  emissions were found to increase slightly with increasing pressure due to conversion of  $\text{NO} \rightarrow \text{NO}_2$ . However, recent measurements by Kjaeraard et al. (1996) show no significant  $\text{NO}_2$  emissions at pressures up to 5 atmospheres, and a widening  $\text{NO}_x$  removal window with increasing pressures, in agreement with the model results, Fig. 3.

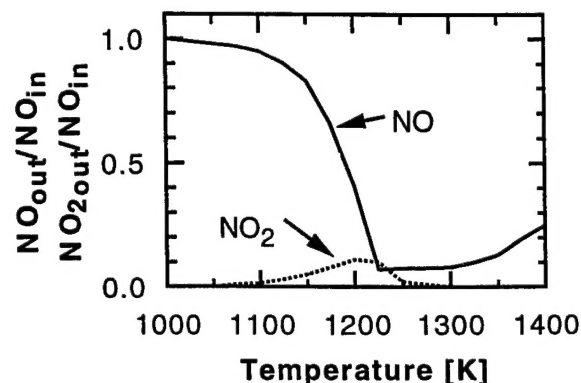


Fig. 3 Calculated NO and  $\text{NO}_2$  in combustion products as a function of temperature for added  $\text{NH}_3$  and a pressure of 20 atmospheres. Initial  $\text{NO} = 225$  ppm; initial  $\text{NH}_3 = 385$  ppm;  $\text{O}_2 = 5.1\%$ ; reaction time = 100 ms.

Figure 4 compares the calculated NO-removal efficiencies for the two reductant types at a pressure of 20 atmospheres for two different exhaust  $\text{O}_2$  levels. The location of the  $\text{NO}_x$ -removal temperature window and the  $\text{NO}_x$ -removal efficiency are strongly dependent on the molecular structure of the reductant species, but only weakly dependent on the  $\text{O}_2$  levels. The differences in the temperature windows are the consequence of the different reaction mechanism for  $\text{NH}_3$  and  $\text{HNCO}$  and are in qualitative agreement with the data of Smith and Caton (1995).

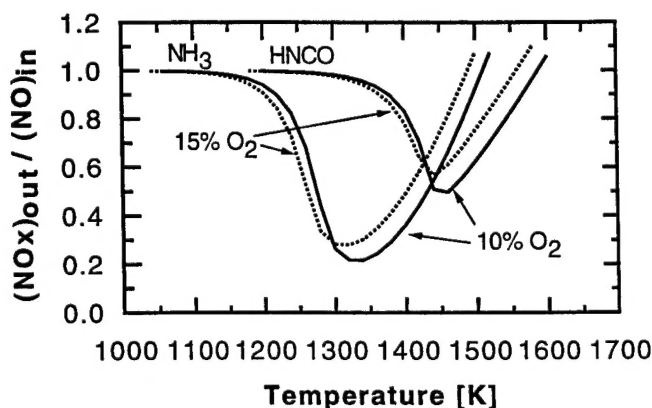


Fig. 4 Calculated reduction in  $\text{NO}_x$  in combustion products as a function of temperature, reductant type and  $\text{O}_2$  levels. Initial  $\text{NO} = 250$  ppm; initial reductant = 500 ppm; pressure = 20 atmospheres; reaction time = 10 ms.



An additional predicted benefit of the SNCR process, Fig. 5, is the consumption of a significant fraction of the residual CO in the combustion products, thereby reducing CO emissions, although there are no experimental data to support this model result.

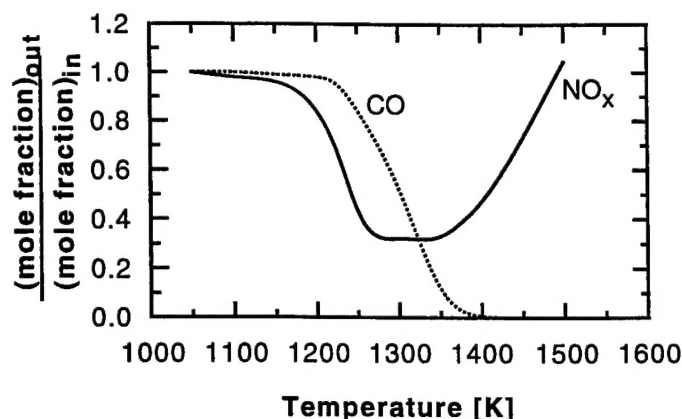


Fig. 5 Calculated reduction in NO<sub>x</sub> and CO in combustion products as a function of temperature for added NH<sub>3</sub>. Initial NO = 300 ppm; initial CO = 600 ppm; initial NH<sub>3</sub> = 600 ppm; O<sub>2</sub> = 15%; pressure = 20 atmospheres; reaction time = 10 ms.

### 3.2 Solid-State Pollutant Sensors

Pollutant sensors play critical roles in control systems for emissions reduction and in compliance monitoring. Of particular interest for control and monitoring of NO<sub>x</sub> emissions is a sensor for NO<sub>x</sub>. The standard method for measurement of NO<sub>x</sub> in combustion gases is based on extractive probe sampling followed by on-line measurement of NO and NO<sub>2</sub> using either a chemiluminescence analyzer or non-dispersive optical analyzers. While quantitatively accurate and species specific, both of these analyzer types have a number of disadvantages, including high cost, the need for periodic calibration, a slow time response, and large size. Hence, there is a need for the development of inexpensive, compact, species specific sensors with rapid time response. Electrochemical transducers represent an attractive class of species sensor that only recently have begun to see application to measurement of regulated pollutants. Most of these sensors utilize thin films of metal oxides and work on resistive changes associated with adsorption of gas on the film. A particularly attractive approach is the combination of the metal oxide sensor with the electrical and electronic elements on a single chip using modern integrated circuit manufacturing techniques. This approach was followed in this phase of the present research effort in order to develop a microelectrochemical semiconductor metal oxide sensor for the measurement of nitrogen oxides in combustion exhaust gases.

## 4.0 Approach

### 4.1 Emissions Reduction by SNCR

Experiments to examine the dependence of  $\text{NO}_x$  removal by SNCR on pressure, temperature, reductant type, exhaust gas composition and reaction time were carried out in a high-pressure reactor, shown schematically in Fig. 6.

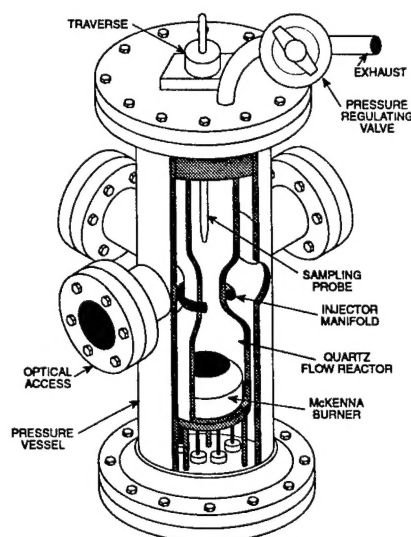


Fig. 6 Schematic diagram of the high-pressure reactor.

A pressure vessel, designed for operation at pressures up to 50 atmospheres, houses a plug flow reactor. The plug flow reactor was employed in the experiments as it allowed investigation of the widest range of temperatures, exhaust gas compositions, reaction times and reductant types. The hot gas source for the flow reactor is a premixed, laminar, flat flame burner. To achieve the desired ranges of exhaust gas composition and temperature, the burner is operated using lean  $\text{CH}_4$ -air mixtures. The nitrogen-containing reductant species, together with  $\text{NO}$ , is injected through six radial opposed jets located at the throat of a converging-diverging nozzle to achieve rapid mixing. The  $\text{NO}$ -removal efficiency depends somewhat on the  $\text{O}_2$  level in the combustion products. To vary the  $\text{O}_2$  levels in the combustion products, additional  $\text{O}_2$  or  $\text{N}_2$  is injected through the jets. A traversing gas sampling or temperature probe is located on the duct centerline. Product gas composition is determined using chemiluminescence, NDIR and ion analyzers. Stable product species measured included  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$  and the reductant to establish reductant slip.

Two nitrogen-containing reductants,  $\text{NH}_3$  and  $\text{HNCO}$ , are of interest in order to determine the role of the reductant molecular structure on the  $\text{NO}_x$ -removal efficiency. These reductants were chosen because the  $\text{NO}$ -removing radical species ( $\text{NH}_2$  or  $\text{NCO}$ ) are representative of those that would be produced by likely fuel additives, because there is an extensive data base on these species at atmospheric pressure, and because chemical models

for the performance of these reductants have been developed. In the experiments reported here, only  $\text{NH}_3$  was employed.

#### **4.2 Solid-State Pollutant Sensors**

This phase of the research program comprised two primary efforts: (1) design and fabrication of an integrated metal oxide sensor for  $\text{NO}_x$  in combustion gases and (2) testing of the sensor for sensitivity, selectivity, stability and time response in simulated combustion products.

The sensor design is based on the technology utilized in the design and fabrication of metal oxide semiconductors. A key feature in the sensor design is selection of the metal oxide film. The desirable characteristics of the film include excellent sensitivity and selectivity for the species of interest and good time response. The most commonly used metal oxide for microchemical sensors,  $\text{SnO}_2$ , shows excellent sensitivity to combustible gases, CO and  $\text{NO}_x$ . However, this broad-based sensitivity results in poor selectivity. The selectivity of  $\text{SnO}_2$  to NO, can be marginally improved by doping with metals such as Ga, Al or In. The metal oxide adopted here is  $\text{WO}_3$ . Recent studies (Akiyama et al., 1993) have shown  $\text{WO}_3$  to be both sensitive to and selective for  $\text{NO}_x$ . A typical transient response of  $\text{WO}_3$  films to  $\text{NO}_x$  is shown in Fig. 7. There is a tradeoff between time response and sensitivity, and the sensor surface temperature plays a key role in this tradeoff. Hence, control of the sensor surface temperature is a critical feature of the sensor design.

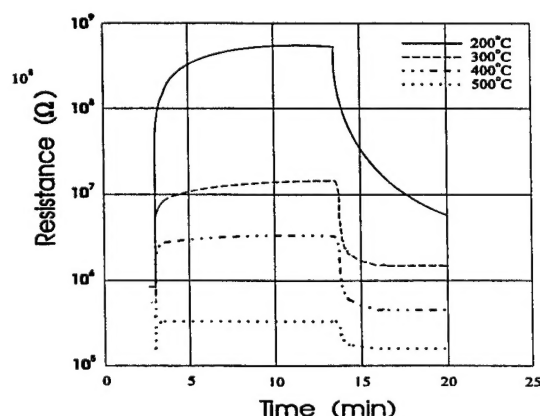


Fig. 7 Transient response of a  $\text{WO}_3$  film to 200 ppm NO in air as a function of film temperature (Akiyama et al., 1993).

### **5.0 Results**

#### **5.1 Emission Reductions by SNCR**

An initial experiment using  $\text{NH}_3$  as a reductant was carried out in the flow reactor at atmospheric pressure to verify experimental procedures. The measured reductions of NO as a function of temperature are compared with model predictions in Fig. 8; the

conditions of this experiment are listed in the figure caption. Good agreement between the data and model results is observed. For the conditions of this experiment, measured  $\text{NO}_2$  mole fractions were always below 2 ppm.

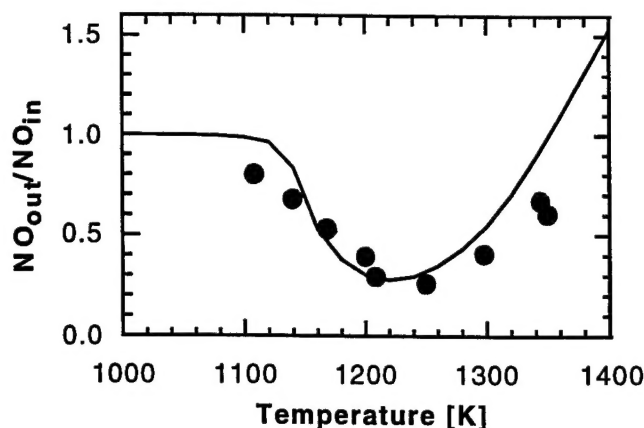


Fig. 8 Comparison of measured and calculated NO removal from combustion products for injected  $\text{NH}_3$ . Initial NO = 100 ppm; initial  $\text{NH}_3$  = 385 ppm;  $\text{O}_2$  = 5.1%;  $\text{H}_2\text{O}$  = 7.3%;  $\text{CO}_2$  = 3.6%; balance =  $\text{N}_2$ ; nominal reaction time = 100 ms; pressure = 1 atm.

Following completion of the atmospheric-pressure validation tests, experiments were conducted at a pressure of two atmospheres. Results from these experiments are shown in Fig. 9, together with the model predictions. Again, good agreement between the model results and data is observed. Similar to the atmospheric-pressure experiments, measured  $\text{NO}_2$  mole fraction were below 2 ppm. Comparison the NO-removal efficiencies of Figs. 8 and 9, indicates a modest widening of the NO-removal window toward higher temperatures, in agreement with model predictions.

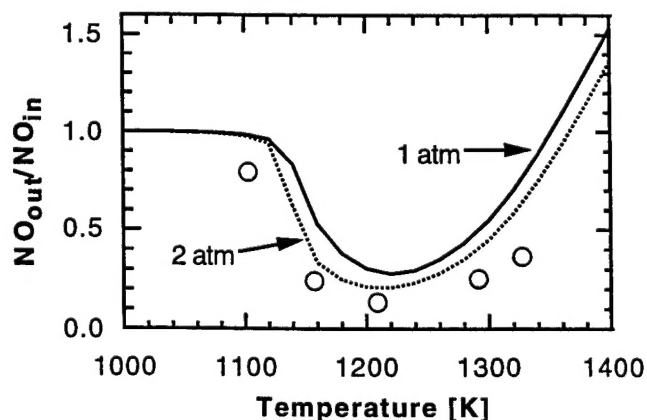


Fig. 9 Comparison of measured and calculated NO removal from combustion products for injected  $\text{NH}_3$ . Conditions identical to Fig. 8, except pressure = 2 atm. Solid line shows model results for a pressure of 1 atm.

## 5.2 Solid-State Pollutant Sensor

A schematic diagram of the solid-state  $\text{NO}_x$  sensor design is shown in Fig. 10, and a photomicrograph of a fabricated sensor is shown in Fig. 11. The sensor is a thin tungsten oxide film on a sensor body that comprises aluminum electrodes, an aluminum temperature sensor and a PECVD (plasma enhanced chemical vapor deposition) polysilicon heating element. The integrated temperature sensor and heater maintain the film temperature at a prescribed level that is independent of the combustion gas temperature. The sensor body is suspended above a silicon substrate to provide good thermal insulation using four  $\text{SiO}_2$  beams. The electrical connections to the heating element and sensor are routed over these beams.

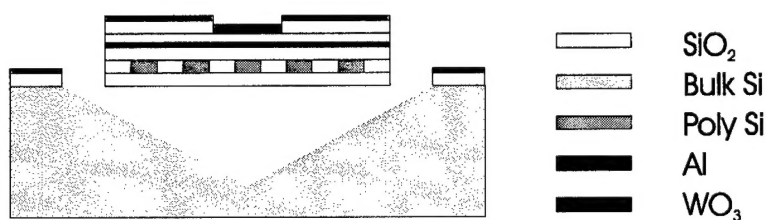


Fig. 10 Cross-section of the solid-state microchemical  $\text{NO}_x$  sensor.

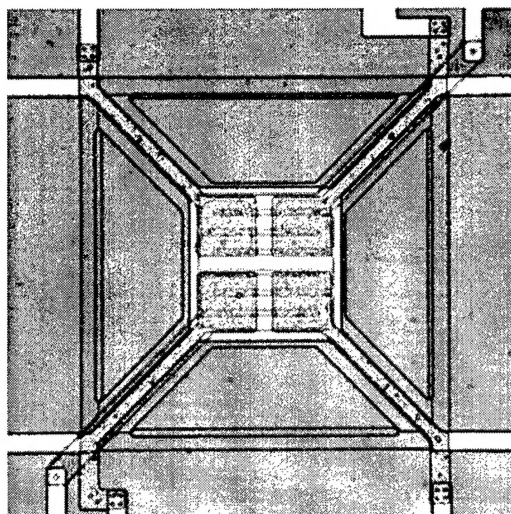


Fig. 11 Photomicrograph of the solid-state microchemical  $\text{NO}_x$  sensor.  
The overall dimensions of the sensor are  $200\text{ }\mu\text{m} \times 200\text{ }\mu\text{m}$ .

The first stage of the sensor manufacturing, involving deposition of all films except the tungsten oxide film, was completed at a commercial foundry. The subsequent manufacturing steps, including etching to remove material under the sensor body, sputtering of the  $\text{WO}_3$  film, and bonding were carried out in the Center for Integrated Systems at Stanford University.

Following fabrication, the sensor was tested in simulated combustion products to establish sensitivity, selectivity and time response. Preliminary tests with this sensor design shows excellent sensitivity for NO and  $\text{NO}_2$ .

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